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Laser Processed Black Silicon for Photovoltaic Applications

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Abstract

We present a femtosecond laser pulse process that induces a texture-like surface structure on silicon wafers and optionally incorporates sulfur into the silicon lattice for emitter formation depending on the processing atmosphere. Such laser processed Black Silicon provides an easily adjustable surface roughness for good light trapping in silicon solar cells. The structure is independent of the silicon crystal orientation and is easily applied on one wafer side only. A sulfur emitter can be formed within the laser structuring process, and allows electric current extraction from a solar cell structure manufactured from this material. Then the advantage is that no further emitter formation step like diffusion is necessary compared to other Black Silicon solar cell approaches, where the Black silicon is created wet chemically. By incorporating sulfur in the silicon crystal lattice, we can show that this Black Silicon absorbs in the infrared wavelength regime. This characteristic can potentially be used to better exploit the energy in the sun spectrum. We manufacture a laser processed Black Silicon solar cell prototype without any emitter diffusion step and achieve the highest efficiency of 4.5 % reported for this cell type.

Keywords: Black Silicon; Femtosecond Laser Pulse; Laser Processing; Single Side Texture; Multicrystalline Silicon Solar Cell

1. Introduction

Nanostructuring silicon is a method for obtaining new material characteristics. Established structuring methods for optimized light trapping purposes are reactive ion etching (RIE) [1] and wet chemical processes [2]. However, these processes only allow limited variations in realizable microstructures, consume toxic gases or chemicals, and are difficult to implement when area selective, single side or homogenous structuring of multicrystalline silicon is necessary like in advanced solar cell structures [3].

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A new approach is using highly energetic laser radiation. When a silicon surface is irradiated with femtosecond laser pulses of a fluence in the range of 20 kJ/m², cones on the micro to nanometer scale are formed at the surface [4,5]. As light is perfectly trapped between the cones, nearly no light is reflected, and the surface appears black. Carrying out the laser process under a sulfur containing atmosphere leads to below band gap absorption due to multiple photon absorption [6].

Nano- and microstructuring silicon by femtosecond laser pulses [5] can be used for tailoring optical [7] and electronic properties [8] without the drawbacks of RIE and wet chemical approaches. The femtosecond laser process allows a high variability in process parameters and permits the realization of a wide range of surface structures. The surface morphology ranges from a wafer like structure to sharp conical spikes, which is also referred to as Black Silicon [9,10]. Furthermore it is possible to incorporate other elements like chalcogenides into the silicon lattice for doping and functionalization purposes [7,11]. Laser processing in a sulfur containing atmosphere significantly increases infrared absorption [12] of silicon at wavelengths above 1100 nm.

2. Experimental

We generate femtosecond laser pulses with a duration of 80 fs by using a Coherent Mantis seed laser and a Spitfire amplifier from Spectra Physics with a repetition rate of 10 kHz at a wavelength of $\lambda = 800$ nm. The processed substrates are boron doped p-type (100) Czochralski grown silicon with a base resistivity of 1 Ωcm. The laser fluence is $F \approx 20$ kJ/m^2.

3. Structural and optical properties of Black Silicon

Irradiating the silicon surface with 500 femtosecond laser pulses under SF_6 atmosphere without moving the xy-stage yields a circular area of cone like spikes, which arise below the original silicon surface. A scanning electron micrograph of such a laser irradiated surface is shown in Figure 1(a) – (c) in different magnifications. Moving the xy-stage in our setup allows to prepare structured areas of any size by scanning the laser spot with some overlap line by line across the sample.

Reflection curves for laser processed surface structures are shown in Figure 2 for different numbers of laser pulses that are applied. An increasing number of laser pulses decrease the reflection. The reason is an optimized light trapping due to the increasing structure feature heights for increasing laser irradiation. The structure morphology will be seen in Figure 3. It is revealed that the structure irradiated with the highest number of laser pulses features the lowest reflection.

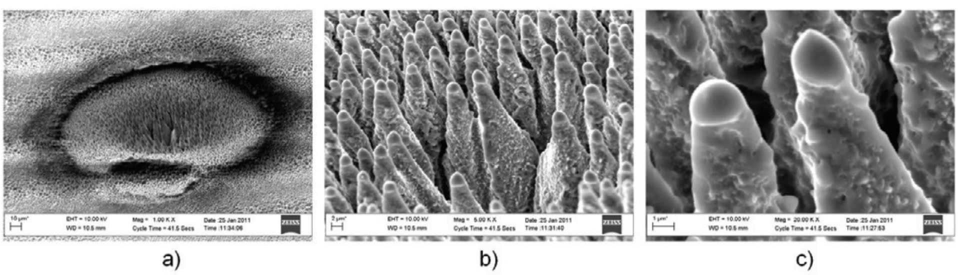

Fig. 1. Scanning Electron Micrograph of a silicon surface irradiated by 500 laser pulses without moving the sample (a) 1k magnification; (b) 5k magnification; (c) 20k magnification

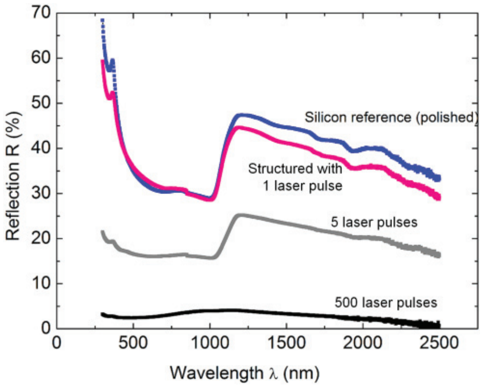

Fig. 2. Reflection of differently structured silicon

4. Applications of Black Silicon

4.1. Single side laser texture for multicrystalline silicon wafers

Varying the number of pulses per laser spot and the laser fluence permits to produce surface features of nearly arbitrary height as shown in Figure 3. In Figure 3(a) only one pulse is applied. Apart from some ripples, the surface remains flat. Using five laser pulses yields a structure like a slightly agitated water surface as shown in Figure 3(b). It is called Grey Silicon. Increasing the laser fluence and maintaining the number of pulses in Figure 3(c) creates a structure comparable to a wet chemical random pyramids texture. With 500 pulses per spot, cone-like spikes form at the surface as displayed in Figure 3(d). This is Black Silicon.

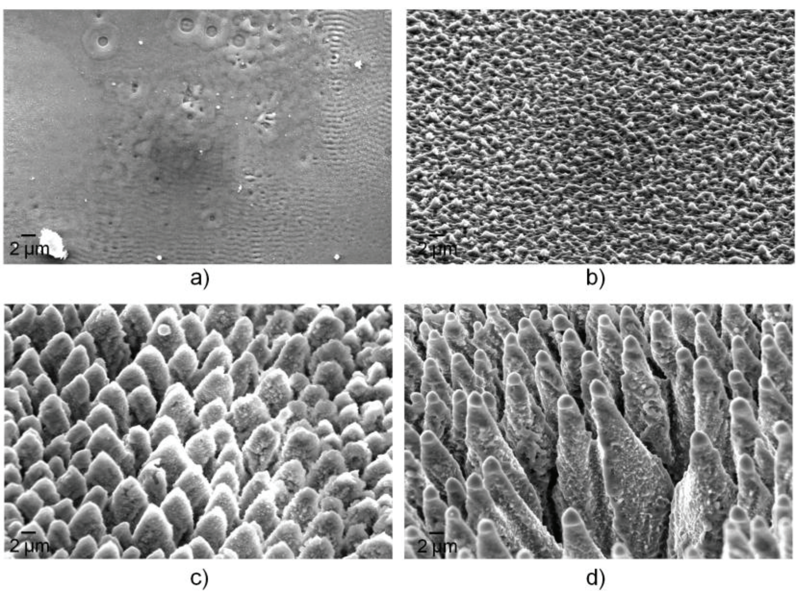

Fig. 3. Scanning electron micrographs from samples processed with (a) 1 laser pulse per spot, (b) 5 pulses, (c) 5 pulses with increased laser fluence, and (d) 500 pulses

These scanning electron micrographs show that the femtosecond laser pulse process can produce a great range of different surface morphologies. As the structuring is performed by laser, this texture method can easily be used for a single side texture or area selective structuring. The adjustable surface features can be created independently of the crystallographic silicon orientation and hence this laser process is well suited for a single side texture of multictystalline silicon wafers.

4.2. Laser doping for emitter formation

By incorporating sulfur into the silicon, an n-type emitter can be formed. The advantage is that the laser process time scales are in the femtosecond regime, which drives the system of sulfur and silicon far from equilibrium conditions [13] and therefore allows for so-called hyperdoping, which permits to incorporate more sulfur into the silicon than it is allowed by its equilibrium solubility of $4\cdot 10^{16}$ cm^{-3} [14]. We measure the sulfur doping profile with Secondary Ion Mass Spectroscopy (SIMS) and calculate the appropriate sulfur concentration of a sample structured in a SF_6 ambient silicon with 5 pulses per spot. The results are shown in Figure 4(a). The sulfur concentration is 0.65 at.% at the surface and decreases to half of this value at a depth of 8 nm and vanishes at 40 nm.

4.3. Infrared absorption

Figure 4(b) presents the absorptance of Black Silicon in comparison to an unstructured silicon reference. A 280 µm thick wafer with Black Silicon texture absorbs more than 95 % of the incoming light for wavelengths in the range 250 nm < λ < 2500 nm. The absorption at the wavelength range above 1100 nm, which corresponds to photons with an energy smaller than the band gap energy of silicon of 1.1 eV, is due to energy levels created by the sulfur. This can be seen from other experiments, where the structuring is performed in vacuum and no sulfur is present [15].

4.4. Femtosecond laser pulse processed Black Silicon solar cell

We use the presented laser process for the fabrication of a laser processed black silicon solar cell. As the laser process accomplishes the surface structuring and the emitter formation simultaneously, the number of processing steps is significantly reduced compared to the fabrication of a standard industrial aluminum back surface field silicon solar cell as shown in Figure 5(a).

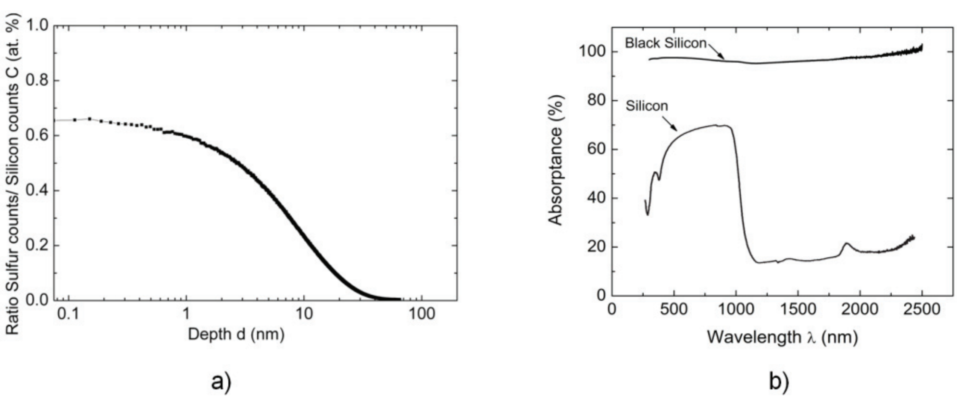

Fig. 4. (a) Depth profile of the sulfur concentration of Grey Silicon determined by Secondary Ion Mass Spectrometry (SIMS); (b) Absorption of differently structured silicon wafers. The wafer thickness is 280 µm

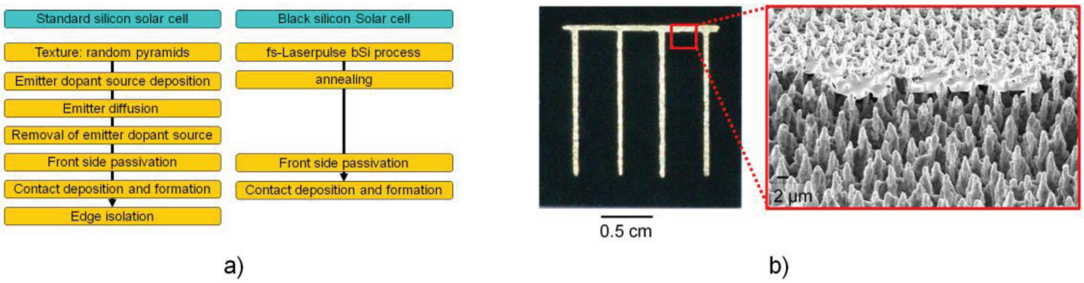

Fig. 5. (a) A comparison of the fabrication process for standard silicon solar cells (left) with that of black silicon solar cells (right); (b) Femtosecond laser processed Black Silicon solar cell and a scanning electron micrograph of the surface structure and the deposited metal contact

By depositing metal contacts on the front and rear side, we achieve the highest efficiency of 4.5% for a laser processed Black Silicon solar cell without front side coatings for antireflection or passivation purposes. So far, laser processed Black Silicon solar cells only reached 2.2 % efficiency [16]. Figure 5(b) presents our Black Silicon solar cell together with a magnification of the silicon surface and the deposited metal contact.

Currently we texture 1cm² in approximately 6 minutes. By using a laser with more output power, the beam can be expanded to more than 80µm in diameter. Currently spot sizes of up to 1 cm² at a fluence of 20 kJ/m² are achievable with pulsed lasers, resulting in a structuring speed of 55 cm² in one second.

5. Conclusions

We show how femtosecond laser pulses can be used for structuring and doping silicon substrates. We investigate structural and optoelectronic characteristics of this material. We find it to be suitable as substrate in solar cell structures. Especially the structuring represents an interesting texture process for multicrystalline silicon, as the surface structure is independent from the silicon crystal orientation. We manufacture a laser processed Black Silicon solar cell and can show an efficiency of 4.5 %, which is the highest efficiency reported for this cell type.

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